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# Process Changes to DWPF to Increase Throughput and Incorporate Salt Streams

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## Abstract

The Defense Waste Processing Facility (DWPF) has been vitrifying High Level Waste sludge since 1996. Sludge batch 1a, 1b, 2, and 3 have been successfully stabilized. In the last several years, the Savannah River National Laboratory (SRNL) has worked with DWPF to implement process and compositional changes to improve throughput. These changes allowed significant increases in waste throughput for processing of sludge batch 3 and will be necessary to maintain reasonable throughput for Sludge Batch 4 (SB4). SB4 processing was initiated in June 2007 and will be the first significantly HM-type sludge batch processed. This sludge is high in aluminum and other components troublesome to DWPF processing. In addition, coupled processing is scheduled to start in the next fiscal year, which will also impact throughput. Coupled processing will begin with the incorporation of waste streams from the Actinide Removal Process and the Modular Caustic Side Solvent Extraction Unit and will eventually transition to the feed from the larger scale Salt Waste Processing Facility. A discussion of the programs to improve throughput and implement salt processing will be provided.

## Introduction and Background

The Savannah River Site (SRS) is currently storing 38 million gallons of radioactive waste in 49 storage tanks. The tank waste consists of two primary forms: sludge and salt. The sludge consists of the insoluble solids fraction of the High Level Waste (HLW) and must be stabilized by conversion to borosilicate glass in the DWPF. Approximately 55% of the radioactivity is present in the sludge fraction. The salt can be present in three different forms depending on the treatment that it has undergone or the storage conditions experienced. The three forms include supernate, concentrated supernate, and salt cake. The salt material must be treated to remove the Cs and actinides to allow stabilization in a grout form in the Saltstone Facility. The plan is to transfer the Cs and actinide containing streams to the DWPF for vitrification with the sludge fraction, which will then be considered coupled operations.

The DWPF has been operating in the sludge-only mode since radioactive start-up in 1996. Five different sludge batches have been prepared in that time following a process known as Extended Sludge Processing (ESP). ESP involves the washing and decanting of the sludge and supernate to remove sodium salts. Decanting also allows the solids concentration to be increased to minimize the volume of material to be treated in the DWPF. Components of concern include nitrite, hydroxide, and carbonate, which must be removed in the initial stage of DWPF processing, and sodium and sulfate, which are both glass formulation concerns. The Tank Farm must balance the need to remove the salts, the desire to minimize the volume of wash water introduced in the HLW system, and the rheological requirements for transferring the sludge during sludge batch planning. Once ESP is complete, the Tank Farm is ready to transfer the sludge to the DWPF feed tank so preparation of the next sludge batch can begin.

Due to the high cost of monitoring these tanks and the potential for environmental release, the Department of Energy (DOE) challenged the site to accelerate the treatment of the HLW material. In DWPF, this can be accomplished through increasing the waste loading per canister or increasing the facility throughput. The Tank Farm, on the other hand, can only meet the challenge by minimizing the amount of washing and accelerating sludge preparation to allow the tanks to be emptied more quickly. SRNL research in various technology areas has been assisting with these endeavors.

Over the longer term, realizing any DWPF process improvements will help significantly during coupled operations because of the large volumes of material to be transferred to DWPF once the salt processing facilities begin production. Currently, the melter is the constraining point in the DWPF because the up-front processing steps typically complete their batch processing in 4 days. The melter, on the other hand, typically takes >6 days to complete the processing of one batch. With the introduction of the salt streams, additional boiling will be required to evaporate the salt streams and the melter will not likely be the constraining point.

## Chemical and Process Improvements

For every sludge batch that is processed in DWPF, qualification studies must be performed to ensure that DWPF will meet its Technical Safety Requirements during processing and that the wasteform produced will meet the DOE's Waste Acceptance Product Specifications. After the identification of processing issues with Sludge Batch 2 (SB2), the physical processing characteristics of the sludge have also become a routine part of the sludge batch qualification process and SRNL programs have been developed to improve the technical understanding of these parameters. The processing testing has gained increased importance recently because of the difference in the composition of the material that is qualified in ESP versus the material that is actually processed in the DWPF. These compositions are significantly affected by the large heels that are now left in the DWPF feed tank when the new sludge batch is transferred.

Currently, the SRNL testing includes washing of the sludge to replicate the Tank Farm targeted endpoint, replication of DWPF sludge preparation steps to include the Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) cycles, fabrication and durability testing of the glass made from the qualification sample, frit optimization studies involving paper assessments and melt rate testing, and variability studies with the sludge and selected frit to ensure that the DWPF models apply. Each of these technical areas provides a potential area where improvements may be implemented. The improvements will be categorized in three technical areas: sludge washing, SRAT/SME processing, and glass formulation and processing. Each of the areas will be discussed in detail in the following sub-sections.

### Sludge Washing

Nominally, the sludge washing target endpoints are driven by the total sodium that can be accommodated in the DWPF glass. Since the sodium is potentially present as compounds of nitrite, nitrate, hydroxide, sulfate, and carbonate, the impact of these components on DWPF processing must also be considered. These factors nominally control the chemical composition of the sludge, while the endpoint target insoluble and total solids concentrations control the physical properties of the feed. The solids serve as a reference point for rheology to ensure that the mixing and transfer pumps are able to pump the washed and concentrated sludge.

For the first three sludge batches (Sludge Batch 1a, Sludge Batch 1b, and SB2), the Tank Farm selected nominal washing endpoints to meet DWPF processing constraints and SRNL washed the qualification sample to match the target. During SB2, the Tank Farm inadvertently washed the sludge to a lower sodium endpoint concentration than the qualification sample in SRNL. When the material was processed in DWPF, pumping/transferring problems were experienced and the sludge showed an affinity to entrain air. These rheological problems were not seen in the sample washed by SRNL. Therefore, some of the problems were attributed to the washing endpoint. For SB3, SRNL personnel worked with the HLW planning organization to determine an optimal target endpoint from both a chemical processing and glass formulation optimization perspective. Significant quantities of excess radioactive material were also added, which resulted in a much higher salt content of the feed. To better understand the potential impacts of washing, the qualification sample was obtained early and the Tank Farm washing strategy was mimicked to best approximate the real sludge behavior. Unlike SB2, SB3 was very thin in rheological terms with a higher insoluble and total solids content than previous sludge batches. The sodium concentration was also much higher than previous sludge batches, which was accommodated by adjusting the frit composition. By working with the Tank Farm and the planning personnel, ESP resulted in a sludge batch that had high solids content with high waste loadings and minimal processing problems in DWPF.

For SB4, settling problems were seen almost immediately after transferring the HM sludge to the ESP feed prep tank. The settling rate is important because the HLW tanks must be stirred on a routine basis to release radiolytic hydrogen that builds up in the sludge. The number of days allowed between mixing is called the "Q" time. Conservatism imposed on this calculation for SB4 severely limited both the mass and the washing strategy since slow settling rates increased the time needed between mixing. Therefore, SRNL studies were crucial to help guide ESP to an optimal endpoint. A similar strategy to SB3 was used for qualification with one more parameter being monitored, settling rate. Fortunately, the SRNL studies showed that settling rates did improve after the initiation of washing, and, more importantly, that washing was more efficient than originally projected. This allowed the plant to meet their restrictive "Q" time limits, while also minimizing the wash water introduced in the HLW system. An important difference was noted between the SRNL studies and the Tank Farm washed material. When SRNL washing studies were completed (including the necessary concentrations), the material met the Tank Farm limits for rheology. The Tank Farm washed sludge, on the other hand, exceeded the Tank Farm yield stress limits and had to be diluted with supernate so the sludge transfers could be made. Two viable explanations for the differences exist: the slurry pumps in the tanks reduced the sludge particle size which increased the yield stress or the samples taken from the tank were not always representative since different sampling methods were used.

As a result of these findings, two studies were performed by SRNL to determine the impact of washing on the slurry rheology. Simulant testing evaluated the impact of five different washing endpoints with the SB3 composition as the center point. Rheology measurements were performed on the sludge slurry before and after DWPF prototypical processing and the sludges were also used for melt rate testing. This testing was collectively called the source of alkali testing. The primary finding was that the center point composition and a slightly less washed sludge had optimal rheological properties. The composition that was slightly more washed was considerably thicker after SME processing to the targeted 50 weight percent total solids and could not be pumped by SRNL melt rate equipment. However, when the solids were adjusted such that the insoluble solids matched the less washed material, the yield stress of the SME product decreased to a value similar to that seen for the less washed SME product.[1] Therefore, the source of alkali testing showed that less washed sludge has advantages with regards to rheological properties if a high total solids concentration is desired for melter feeding. The melt rate testing data showed that sodium depletion in either the frit or sludge had a negative impact on melt rate, but the melt rate impact of slight changes in washing could not be discerned.[2]

The second study involved testing with radioactive SB3 slurry at different insoluble solids concentrations and washing endpoints. The measurements were performed to provide insight into potential processing problems that may occur and to provide further insight into the impact of washing on the rheological properties. As expected, yield stress increased with the insoluble solids concentration. At equivalent insoluble solids, SB2 material had a yield stress approximately three times higher than the SB3 material. This difference was attributed to the difference in washing endpoint with a sodium supernate concentration of ~1M for SB3 and ~0.5M for SB2. Lastly, the SB3 material did show a propensity to entrain air at higher insoluble solids concentrations with additional washing.[3]

Therefore, both studies supported the trend to wash less to improve the sludge physical behavior. By adopting this philosophy, the Tank Farm can minimize the wash water introduced to the HLW system to help meet its accelerated closure goal.

**SRAT/SME Processing**

With less washing in the Tank Farm, the DWPF feed preparation processes require more acid to remove or neutralize the salt components. Acid is added in the SRAT to destroy nitrite, reduce mercury and manganese, neutralize hydroxides and carbonates, and adjust rheo logy. Both formic and nitric acids are added with the relative amounts of each determined by a REDOX equation that targets a $Fe^{2+}/\Sigma Fe$ of 0.2. Typically, the higher nitrite also comes with higher nitrate, which is added for corrosion control in the Tank Farm, shifting the split of the acids more to the formic acid side to maintain the REDOX ratio. The negative side of this process change is the potential increase in hydrogen generation from the increased formic acid addition (hydrogen is generated from the catalytic reaction with the noble metals in the sludge) and higher offgas emissions in the facility from the decomposition of the salts and acid. As mentioned above, the positive side is that rheology is typically improved with the presence of the salts even at higher solids concentrations. Hence, SRNL testing is performed to provide an acid operating window that completes the necessary reactions while staying below the flammable limit for hydrogen. SRNL programs have also been initiated to better understand the catalytic reaction and to improve the prediction of the acid addition requirement to minimize the potential impacts on the DWPF.

While acid addition can be used to influence the rheology, as was done in SB2, alternative additives/changes would be preferred to minimize the melter cold cap reactions. The physical design of the facility is difficult to change because of the requirements for remote handling and maintenance. Thus far, the change that appears to have the most promise and the least negative impact on the process is the use of glass beads instead of frit particles. SRNL testing has shown that the rheological properties of simulant melter feed containing 90% spherical frit (beads) particles were less viscous compared to DWPF melter feed containing irregular shaped frit particles.[4] The lower rheological properties have the potential to allow a higher total solids concentration to be processed, which minimizes the water that has to be evaporated in the melter. However, before this change can be implemented in the DWPF, evaluations of the processing impacts of changing the frit have to be completed especially given the potential to change the wasteform or glass composition.

Potential processing impacts for implementing beaded frit include changing of the melter feed settling rate, which effects mixing and sampling of the melter feed slurry and the frit addition equipment, and the melt behavior due to decreased surface area of the beads versus frit. In the initial SRNL evaluations, beads were produced from DWPF process frit by fire polishing. Figure 1 shows a picture of the fabricated material, with ~90% of the frit converted to beads, and the typical process frit.[5] Melter feed slurries were prepared by combining sludge simulant with the prepared beads. The yield stress of the feed with beads was compared to the yield stress of the feed with frit. A Haake rheometer was used for the measurement and the data was fitted to a Bingham Plastic model. Two different sludge simulants were used and the data showed that the melter feed containing beads had a yield stress decrease of 20 to 40%.[5]

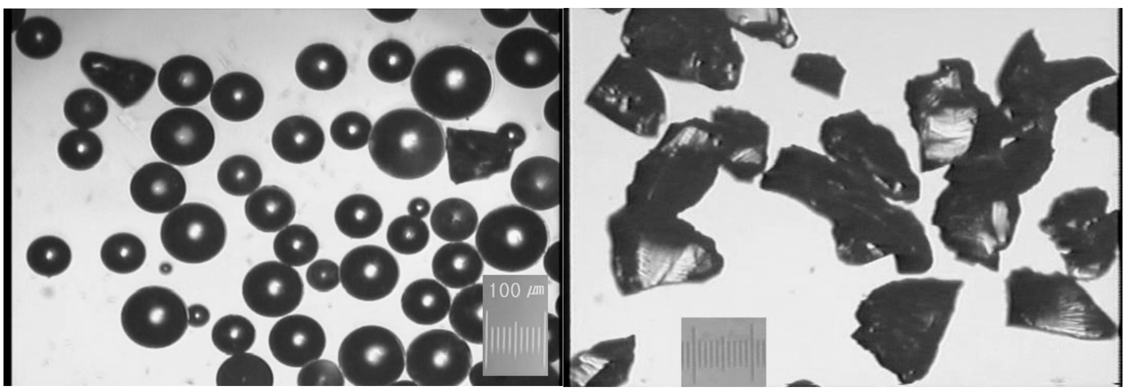


*Figure 1 SRNL Beaded Frit and DWPF Process Frit*

For prototypical frit, the particle size specification (+80/-200 mesh) was derived to minimize the impact on the melter feed yield stress. Smaller particle size was shown to increase yield stress. The impact of this change was evaluated for the beaded frit. The size of the particles was selected by matching the settling rate of the beads with the settling rate of the frit. Table 1 shows the rheological properties of beaded frits of different particle size compared to the standard DWPF frit. [5] Improved rheological properties are seen across all particle size ranges tested with the beaded frit.

**Table 1 Impact of Frit 320 and Various Sized Beads on Rheology of SB3 SME Product [5]**

| Frit Type | Particle Size (mesh) | Yield Stress (Pa) | Consistency (cP) |
|---|---|---|---|
| DWPF Frit | -80/+200 | 3.26 | 20.53 |
| Beaded | -140 | 2.64 | 16.05 |
| Beaded | -100/+140 | 2.51 | 15.27 |
| Beaded | -70/+100 | 2.61 | 12.88 |

To assess the impact on feed settling, settling tests were conducted with water, xanthan gum solutions, and HLW simulants. HLW simulant testing used a slurry at 45% total solids. The testing showed that beads settled slightly faster than frit at a given particle size. However, the testing also showed that a smaller bead particle size (e.g. -100/+140 mesh) could be used to obtain slower or equivalent settling rates to standard frit (e.g. -80/100 mesh). This allowed the target particle size of the beads to be reduced to -100/+200 mesh.[5]

The frit addition system was evaluated by conducting flow loop testing. This involved the fabrication of a prototypical melter feed loop with an ~9 m clear PVC pipe recirculation loop with a small feed tank and Jabsco pump. A bypass return loop was installed immediately after the pump and instrumentation for measuring flow and pressure were installed on the outlet side of the pump.[5] The system tested solutions of both -100/+140 mesh beads and prototypical frit at typical solids loadings. Data recorded during the testing included pump power, flow rate, and outlet pressure, while observations of the flow in the horizontal section of the loop were noted. By adjusting the recirculation flow, the minimum flow for avoiding settling was observed in each test. This testing was successfully performed for bead solutions at 50, 55, and 60% total solids. However, the testing with prototypical frit was only performed with the 50% mixture due to pump impeller failure attributed to the erosive frit particles.[5] For the same flow rates, the data showed increased line pressure as the solids increased and with prototypical frit. A comparison of the measured line pressures versus velocity for the four tests indicated equivalent inflection points for the bead and frit solutions providing a preliminary indication that the bead slurry would not require higher flows rates than frit slurry at DWPF during transfers. An additional positive observation was the ability to re-start pumping of the bead slurry after flow had stopped. This could not be performed with the prototypical frit slurry because it showed a propensity to pack tightly when settled.[5]

To initiate melt rate assessments for this process change, sufficient melter feed simulant was fabricated using beads and frit to produce 500 grams of glass. The materials were tested in the Melt Rate Furnace (see discussion below for a description of this system) and the measured melt rates were nearly identical. Differences were seen in the appearance of the surface and the beaded material seemed to show more offgas entrainment.[5]

Although the beaded frit has shown very promising results to date, additional testing is still required before it can be implemented in DWPF. In the next six months, SRNL testing will assess the following:

- Flowability of the beads through the dry feed frit system, including the simulation of vertical and horizontal plugging situations to determine the ease of remediation;
- Impact of the bead/frit ratio on processing since frit will still be needed for canister decontamination (which is recycled to the DWPF process);
- SME processing and Hydragard sampling impact, homogeneity and the ability to obtain representative samples must be maintained; and
- Melter processing impacts to include slurry fed testing to evaluate cold cap reactions.

Planning for this work has been initiated.

## Glass Formulation and Processing

Once the sludge tanks are selected for the sludge batch, no opportunity exists to change the composition of the major sludge components. The sodium content can be changed through the washing process, but the other major oxides are not removed during the washing process so the blend of sludges must represent a feasible sludge option. The glass composition, however, can be changed and optimized through the judicious selection of the frit composition.

Before DWPF started up, several frits were studied to provide optimum operating conditions for the seven Waste Compliance Plan projected sludge compositions. Frit 202 was the primary candidate for coupled operations and it was combined at 28% waste loading with the frit and PHA to provide seven projected glasses compositions. These glasses met the DWPF processing and durability constraints. However, the sludge compositions assumed considerable blending and Al-dissolution would be pursued after DWPF began operation. With the DOE challenge to accelerate closure, neither of the assumptions is valid, and waste loadings >28% are desired plus the salt processing strategy has also been changed.

Given these changes, SRNL programs were initiated to pursue tailored frits for each sludge batch. The goals were to find a frit to improve melter throughput and the upper limit on waste loading. While the impact of the frit composition changes on the waste loading window and the predicted processing properties can be successfully assessed through calculations, estimating the impact on melt rate or throughput is not as straight forward. Historical melter testing at SRNL and actual DWPF operations have shown that higher waste loadings can result in operational problems including lower melt rates and large pressure spikes in the off-gas system. The low melt rates can contribute directly to low throughput, while pressure spikes can cause pluggages of the melter pour spout and bellows liner and increase the potential for large masses of glass to be siphoned out of the melter. These scenarios contribute indirectly to low throughput because they cause operational down time for cleanouts and lower overall facility attainment. Hence, SRNL needed to develop tools to ascertain the potential impact of the frit and process changes from a throughput and operational perspective. The next sub-sections discuss both types of assessments.

***Paper Assessments of Operating Window***

The objective of the paper assessments is to provide the technical information needed to select a frit for processing. The key criteria or aspects that are used include:

- Size of the projected operational window in terms of waste loading over the anticipated sludge composition region upon combining with the frit;
- Robustness of the operating window to anticipated sludge composition variation;
- Ability to improve or maintain high waste loadings through the use of the frit;
- Relative ease in fabricating the frit composition (i.e., melt temperature of the frit can not be excessive since the material must be supplied by a vendor in mass quantities and then the frit must easily re-melt at 1150ºC); and
- Ability to improve or maintain high melt rates.

The paper study assessments are used to assess the first three items, while experimental studies must be performed to assess the last two criteria. Normally, two stages are used in the assessment: the Nominal Stage and the Variation Stage. A more thorough description of the process is provided in WSRC-TR-2002-00491 by D.K. Peeler and T.B. Edwards [6]. In summary, the Nominal Stage utilizes the nominal sludge composition(s) and candidate frit compositions to determine the ability to provide a reasonable operational window. Glass compositions are developed over the waste loading interval of interest, typically 25 – 60 weight percent, and property predictions are performed using models currently implemented in the DWPF. The primary property predictions assessed include liquidus temperature, viscosity, and durability, but glass solubility limits are also considered. The results can be used to quickly screen options provided by the HLW planning organization.

Given that this stage does not investigate sludge composition variation, an increased risk in processing or for product quality would result if the frit or sludge preparation option decision was based solely on the Nominal Stage assessment. Hence, the intent of the Variation Stage assessment is to gain insight into the robustness of the candidate frits with respect to compositional variation. The number of data points generated when this variation is considered is large, so the Variation Stage is not typically initiated until the frit or sludge options have been minimized. Statistical mixture experimental design methods are then used to obtain an initial set of feasible compositions bounding the sludge region(s) of interest. The methods include algorithms that can be used to determine the extreme vertices (EVs) of a sludge region (the bounding compositions). Typically, the JMP software package [7] is used to generate the EVs for the region of interest. Once the EVs and centroid compositions are determined, evaluations are made using the same DWPF models used in the Nominal Stage assessment. However for this stage of the assessment, the predicted properties are evaluated using the more restrictive Measurement Acceptability Region (MAR) limits.

Use of the Nominal and/or Variation Stage assessments is generally an iterative process as compositional projections are updated (e.g., analysis of actual tank sample are accounted for or blending/washing strategies are refined). The output is the identification of primary frit(s) to be used with the sludge composition or blending/washing strategy assessed. While it can be advantageous to develop a frit that is robust to large compositional regions, the disadvantage is the non-optimization of the frit composition in terms of other processing criteria (such as melt rate or waste throughput).

***Melt Rate Testing***

Two different melt rate tools have been developed and continue to be used for evaluating process and frit changes. The first is the dry-fed Melt Rate Furnace (MRF). The MRF is primarily a scoping tool that uses dry feed to evaluate melt rate differences between different feeds. The furnace has a cylindrical inner chamber with heating coils winding around the chamber walls with an insulating sleeve. The measurements are typically performed at 1150°C. In a typical test, sufficient feed to produce ~ 500 grams of glass is placed in a 1200 mL stainless steel beaker. Once the furnace reaches temperature, the beaker is inserted from the top and the beaker is lowered so that the bottom is typically flush with the top of the uppermost chamber coil. An insulating block is used to cover the beaker. After the prescribed residence time, usually 50 minutes, the beaker is removed and is allowed to slowly cool to room temperature. Melt rate is assessed by sectioning the beaker and measuring the height of glass formed along the bottom of the beaker. The measurement can also be performed by x-raying the whole beaker and measuring the height of glass from the radiograph. Both methods provide linear melt rates for the feed system. This testing has been shown to accurately predict the impact of frit composition and waste loading changes, but has been less successful at accurately predicting the impact of changes such as acid amounts since the material is dry when placed in the beaker. Throughput curves that have been generated as a function of waste loading have also been successful in predicting the relative behavior during DWPF processing. Typically, these curves show an optimum waste loading peak for the feed at a given waste loading. While the exact value may be slightly different in DWPF (typically slightly lower waste loading percentage in DWPF), the trends typically hold.

The other melt rate tool is the Surry Fed Melt Rate Furnace (SMRF), which is used to compare melt rates between slurry feeds and to provide limited cold cap behavior evaluations. Typically, SMRF testing is performed after the feeds have been tested in the MRF and options have been narrowed down. The MRF is typically used as the discriminator since it requires much less feed and less time to complete testing. The SMRF is designed to mimic the heat transfer characteristics of the DWPF joule-heated melter. This is accomplished by providing heating in one dimension through the bottom of an ~20 cm diameter Inconel 690 crucible. Insulation is used around the sides of the crucible in the melt pool area to minimize radial heat transfer and heat exchange with the plenum. This mimics the heat flow that would be present in a large melter that relies on convective and conductive heat transfer between the glass pool and cold cap. The glass temperature is controlled by a thermocouple contacting the bottom of the crucible and is maintained at the temperature set point of 1125°C. Additional heating is applied to the plenum by Globar® heaters that surround the top of the crucible. The heaters are controlled to simulate different plenum conditions in the DWPF melter, and the temperature is controlled by a thermocouple in the vapor space. Glass is discharged from the system through a pour tube that is equipped with induction heating on the lower 7.5 cm of the pour tube.

Feeding to the SMRF is automated and based upon maintaining a constant plenum temperature set point. After each feed cycle, the feed controller waits for the melter to return to the plenum set point temperature for feed cycle initiation. Typical feed cycles take ~20 seconds and deliver about 100-110 grams of feed. As the automatic feed system dispenses slurry feed onto the melt surface, glass is continuously poured through the overflow pour tube. The poured glass is collected in a catch pan located beneath the pour tube discharge. Melt rate is assessed by weighing the amount of glass poured from the SMRF over the test period. The SMRF has been shown to provide fairly accurate predictions of feed behavior in the DWPF melter. Like the MRF, the predictions are relative and not absolute measurements of melt rate. The SMRF can be used to assess the impact of waste loading, frit composition, and acid strategy. It has also been used to measure glass solubility limits for troublesome components such as sulfate and titanium oxide. The SMRF is, however, limited by the feed system and the crucible size. The cold cap surface area greatly limits the amount of feed fed per unit time.

For several years, the SMRF has been the final melt rate tool used before providing recommendations to DWPF regarding process variables. With the feeding and cold cap limitations, a larger melt rate tool, the Cold Cap Evaluation Furnace (CEF), was needed to adequately investigate cold cap behavior. The CEF was designed specifically to provide better visual observation and measurement of cold cap properties. These include feed flow, cold cap thickness, mounding, and foaming tendencies. The goal is to eventually modify the CEF such that problematic melter off-gas surges could be investigated. The CEF consists of an ~51 cm diameter and ~43 cm tall Inconel® cylinder heated from the bottom with four external electric elements. The vapor space is heated using four electric elements located inside alumina protection tubes. It is equipped with a pour and drain tube that are heated with cylindrical resistance heaters.

To date, an initial checkout of the CEF has been performed using glass cullet and melter feed with known processing properties. The vapor space heaters have been tuned during each run to ensure the proper response from the vapor space heaters and the feed system. A feed strategy similar to the SMRF has been successfully utilized. Testing showed the need for some improvements to the insulation, which have been made. Thus far, the sight glasses have provided an opportunity for viewing or monitoring cold cap behavior with some cleaning to remove deposits. Additional improvements are being made to this system and it will begin testing with simulant feed in September 2007.

In general, the melt rate tools have been able to provide guidance for frit development and sludge planning efforts. Some of the specific findings include:

- Less washing resulted in a higher melt rate when tested with two different SB3 options;
- Feed REDOX did not negatively impact melt rate until it was below $Fe^{2+}/\Sigma Fe$ of 0.1;
- An increase in acid stoichiometry has the potential to lower melt rate if the system is overwhelmed by free acid (i.e., acid that is not reacted with the feed material);
- Lower melter feed weight percent total solids typically result in lower melt rates due to the need to evaporate extra water; and
- Higher waste loadings typically decrease melt rate but the optimal waste loading target may be different for each sludge/frit system.

Once again, these findings had to be determined through physical testing since no models for predicting melt rate behavior currently exist. Attempts are being made to predict melt rate through the use of an existing DWPF 4-stage cold cap model. More specifically, the cold cap model ranks the relative melt rates of various melter feeds based on two primary outputs: total Gibbs free energy of the final melt and molar flow of calcine gases. Application of the model has thus far correctly ranked differences in frit composition, sludge washing, glass REDOX, and acid addition strategies as compared to results in the MRF and/or SMRF tests. The data from recent runs are being added to the database to evaluate compositional changes on the system.

## Incorporation of Salt Processing Streams

In 2008, the SRS will begin operating its Actinide Removal Process (ARP) and Modified Caustic Side Solvent Extraction Unit (MCU) facilities. These facilities will treat the salt fraction from the HLW tanks until the larger Salt Waste Processing Facility (SWPF) can be brought on-line. The salt fraction will undergo treatment to remove the Cs and the actinides.

The ARP facility will treat the portion of the salt that is low in cesium but high in actinides. The process will involve the addition of monosodium titanate (MST) to HLW supernate to absorb soluble strontium, plutonium, uranium, and neptunium. The resulting slurry, which will also contain entrained sludge, will then be filtered to remove the insoluble solids. The concentrated solids will be washed to reduce the sodium and nitrite concentrations. Upon completion, the MST slurry will be transferred to the DWPF and the filtrate to Saltstone.

The MCU process is based on the Caustic Side Solvent Extraction (CSSX) process that will be implemented in the SWPF being built by Parsons, Inc. The main objective of the MCU process is to remove cesium from the salt, which is accomplished by contacting with an immiscible organic solvent. The organic solvent is a combination of BOB-CalixC6, Cs-7SB modifier, tri-n-octylamine, and the diluent Isopar®L. The waste exiting the contactor bank is considered decontaminated of cesium and is called Decontaminated Salt Solution (DSS). The organic solvent is transferred to the scrub section where the contactors neutralize any alkaline carryover with dilute nitric acid and return any sodium or potassium to the waste feed stream. The solvent then moves to the strip section, which strips the solvent of the cesium and concentrates it in a very dilute nitric acid stream. The stream that exits the strip section contains the cesium and is called the strip effluent. Solvent is recycled and washed with caustic after this step so it can be used for further processing. Both the strip effluent and DSS are sent to decanters to remove any solvent carryover before being transferred to the Strip Effluent Hold

Tank (SEHT) or the DSS Hold Tank (DSSHT), respectively. The strip effluent in the SEHT is sent to the Strip Effluent Feed Tank (SEFT) in the DWPF, while the DSSHT is transferred to the Saltstone feed tank.

Initial assessments of the impact of the ARP and MCU on DWPF processing have been completed at SRNL. The chemical process cell impacts and the glass composition and melter impacts are discussed in the following sections.

**Chemical Process Cell Impacts**

In the DWPF, these streams will be incorporated by adding the ARP stream at boiling to the SRAT before any sampling has been performed but after the sludge transfers have been made. After boiling is completed, the SRAT receipt sample will be taken to allow the adjustment of the acid addition for the acid-consuming materials in the ARP stream. The acid will then be added at 93ºC and the SRAT material will be taken to boiling where concentration will be performed to meet the target total solids. Typical DWPF processing would then reflux the SRAT material at boiling for 12 hours or longer if needed to remove Hg. When MCU strip effluent is processed, reflux will not be performed because the MCU stream will be added at boiling. The SRAT cycle will end once the entire MCU stream is added or after the necessary time needed to remove the Hg.

SRNL studies have shown that these materials will have minimal impact on the physical properties of the sludge material, SRAT product, or SME product. However, processing will require much longer times in the DWPF and the SRAT could end up taking >6 days from the start of ARP incorporation to the end of the SRAT. The SRAT will then be the limiting point in the facility. In addition, the facility will be dealing with higher gamma radiation than it has seen to date because of the Cs-containing MCU stream. The MCU stream will contain a small amount of the organic solvent. This solvent has been shown to accumulate at low concentrations in the SRAT/SME condenser system and may require the facility to clean these vessels more frequently. Once the SWPF comes on line, significantly larger quantities of both streams will need to be processed per batch, which will delay SRAT processing even further. Thus, SRNL and DWPF personnel will continue to work together to evaluate possible improvements that might be made to the facility or the process to minimize the impacts of coupled processing.

**Glass Composition and Melter Impacts**

The ARP stream contains two components of interest to the glass composition. The ARP will contain MST, which contains both sodium and titanium. Additionally, sodium will be associated with the aqueous part of the stream from washing and preparation of the stream for transfer. Sodium impacts most of the glass properties and, more importantly, can impact the durability of the final waste form. Titanium dioxide has the potential to impact the glass liquidus temperature or crystal forming potential of the glass. The impact of the ARP levels of sodium and titanium dioxide have been assessed for SB4, and minimal impact on the glass formulation or frit selection was seen. In fact, a slightly higher operating window was seen and the same frit could be used for processing in sludge-only or coupled operations. This provides needed flexibility for DWPF processing since it does not require them to maintain two frits in case the ARP stream is not always available. An initial melt rate assessment has been completed using the MRF and no apparent impact was seen from the ARP levels of titanium dioxide.

The MCU stream will have minimal impact on the glass composition. An evaluation has been completed to ensure that the anticipated Cs-loading in the glass is below the baseline values for safely operating the plant. It is anticipated that more Cs may be emitted to the melter offgas system during MCU processing. Depending on the volume of the solvent carried over to the melter, the potential exists for altering the glass REDOX. Initial studies indicate very small quantities will be carried over, but before DWPF begins processing, the existing DWPF REDOX equation will be updated to ensure that impacts are considered.

The final flowsheet for the SWPF is still being finalized. This flowsheet will need to accommodate much larger quantities of both the MST/sludge solids containing stream and the strip effluent stream. Once these volumes are finalized, SRNL glass scientists will perform the necessary paper and melt rate assessments to ensure that acceptable processing will be possible. The biggest concern is the amount of titanium dioxide being transferred to the facility since DWPF has an existing limit at 2 weight percent titanium dioxide.

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